



Photoluminescence behaviour of Cu doped ZnS Nanoparticles synthesized by wet chemical route method

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Abstract : Cu doped ZnS Nanoparticles in powder form were prepared by wet chemical route method by using thioglycerol as a capping agent. The prepared powder was characterized by using X-ray diffraction (XRD) analysis. The XRD studies indicated that most of the samples are having cubic phase. The absorption spectra, and photoluminescence behaviour of bulk ZnS, nano ZnS and Cu²⁺ doped ZnS have been studied. Absorption spectra of bulk ZnS and nano ZnS is present around 315 nm no shifting in wave length was observed for both. After doping of Cu²⁺ ion the absorption wavelength shifted towards the lower wave length around 290 nm, this blue shift in the absorption edge is a measure of increased band gap. Photoluminescence spectra of pure and doped ZnS were recorded under 256 nm. The emission spectrum of pure ZnS has a blue emission band centred at 440 nm. After doping with Cu²⁺ ion the luminescence centers were transferred to impurity ions. The emission peak of the Cu²⁺ doped samples is centered at 510 nm. The PL intensity of doped ZnS samples increases in comparison to pure ZnS.

Keyword: ZnS, Cu²⁺ doped ZnS, absorption spectrum, thioglycerol luminescence spectrum.

I. INTRODUCTION

Zinc sulfide (ZnS) is a direct transition semiconductor possessing the largest band gap among II-VI semiconductors [1,2]. ZnS-based phosphors activated by transition or rare earth metals are famous materials with diverse luminescence properties, such as photoluminescence (PL) and thermoluminescence (TL) [3-7]. They are currently employed in many areas, including light emitting diodes (LEDs), flat panel displays (FPDs), liquid crystal displays (LED) backlight and cathode ray tube (CRT) equipment [8-10]. This kind of nonmaterial's exhibits unusual physical and chemical properties in comparisons with their bulk material, such as size dependent variation in comparisons of the band gap energy [11,12].

As an important semiconductor material, ZnS is chemically more stable and technologically better than other chalcogenides (such as ZnSe), so it is considered to be a promising host material. Transitional metal ions (e.g. Mn²⁺ [13,14] and Cu²⁺ and rare earth ions [15-17] have been incorporated into ZnS nano-structures by

different synthesis techniques. Two emission bands (blue and green) were often observed together in the same sample, such as 420nm and 520nm by Lee et al. [18] and 460nm and 520nm by Xu et al. [17]. On the other hand, a single emission peak was also observed at 480nm [15] or at 415nm [19]. Recently, Bol et al. reported a red emission around 600nm in ZnS:Cu nanoparticles and assigned it to the recombination between a deeply trapped electron and Cu²⁺ [20-23]. The present paper reports the effect of particle size on Photoluminescence spectra, and optical absorption spectra were investigated.

II. EXPERIMENTAL

The pure and Cu²⁺ doped ZnS nanoparticles were synthesized by a chemical route method. Aqueous solution of zinc acetate, copper acetate and sodium sulphide were used as a precursor material. Thioglycerol was used as a capping agent. Sodium sulphide solution was slowly added to a boiled mixture of zinc acetate and thioglycerol nano ZnS was formed. For preparation of Cu²⁺ doped ZnS; thioglycerol solution was added slowly in zinc acetate and copper acetate mixture. The mixture was heated till boiling and cooled at room temperature followed by slow addition of sodium sulphide solution with continuous stirring in an ice bath. The precipitate of ZnS:Cu²⁺ nano particle was formed and separated by centrifugation of the mixture. The separated powders were repeatedly washed by using distilled water then the samples were dried and used for further investigations.

The X-ray diffraction (XRD) patterns were recorded to characterize the phase and structure of the nanoparticles using a Rigaku Rotating Anode (H-3R) Diffractometer with rotating anode and a Cu K α radiation source ($\lambda=1.5418 \text{ \AA}$). Absorption spectra of the samples were recorded with the help of UV-Visible, Perkin-Elmer Model Lambda 950 Spectrophotometer. Room temperature photoluminescence (PL) of the powder samples was measured to characterize the luminescence properties of the nanoparticles, with spectrofluorometer.

III. RESULT AND DISCUSSION

3.1 X- Ray diffraction (XRD) Results:- XRD patterns of the pure ZnS and ZnS: Cu nanoparticles are shown in Fig. 1. The XRD analysis reveals the cubic zinc blende structure of ZnS (JCPDS No. 05-0566). The three peaks corresponds to the (111),(220), and (311) lattice planes, respectively. From the XRD patterns, the broadening of the diffraction peaks of the nanoparticles is obvious, which is characteristics of nanosized materials. According to the line width analysis of the (111) diffraction peak based on Scherer formula [24-30], the average size of the particle for pure and doped ZnS were estimated in between 5-10 nm [5]. From XRD analysis, no characteristic peaks of impurity phases were observed in doped samples. That is due to very small amount of impurity, and these ions were doped into ZnS lattice.

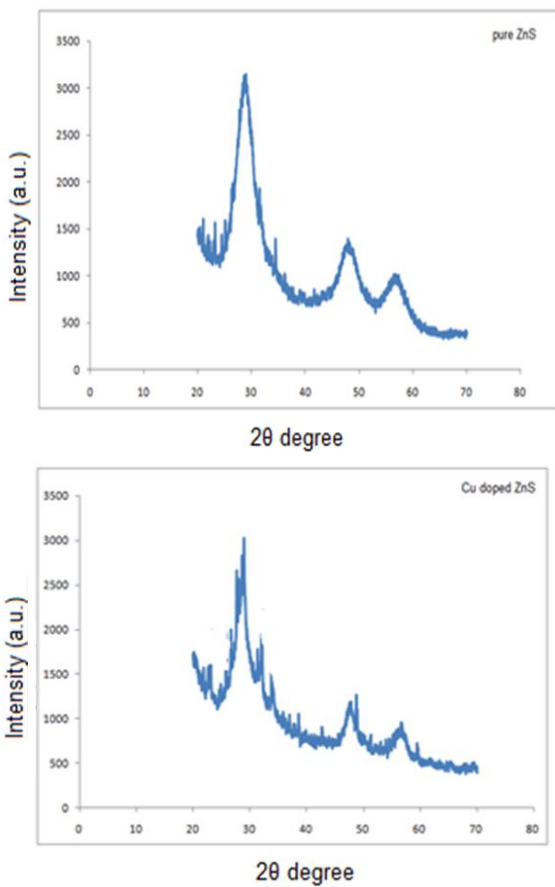


Fig. 1. XRD pattern of the pure ZnS and Cu doped ZnS [5].

3.2 UV-Vis Absorption Spectra Results:-The UV absorption spectra of bulk and nano ZnS and doped ZnS:Cu²⁺ is shown in fig. 2. The bulk ZnS peak is present around 315 nm ($E_g = 3.942\text{eV}$). However, the absorption spectra of nano ZnS and Cu²⁺ doped ZnS samples were observed at 305 nm and 290 nm respectively, which indicated the existence of a narrow size distribution of quantum particles of prepared samples. The band gap of the samples was estimated at about 3.94-4.28eV (Table 1). A slight blue shift in

absorption edge was observed for the absorption spectra of undoped and doped ZnS samples [21,31].

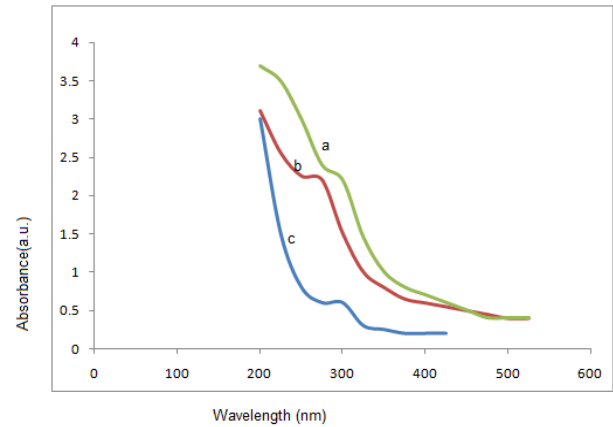


Fig.2 UV-Vis absorption spectra of (a) ZnS pure, (b) ZnS: Cu²⁺, (c) ZnS bulk.

Table 1. Absorption spectra of bulk ZnS, pure ZnS (nano) and doped ZnS: Cu

Samples	Band gap energy (eV)
Bulk ZnS	4.28eV
Pure ZnS(nano)	4.14eV
Doped ZnS:Cu	3.94eV

3.3 Photoluminescence Results:- The photoluminescence emission spectra of bulk ZnS, nano ZnS and Cu²⁺ doped ZnS has been recorded under 256 nm excitation. The emission spectra of bulk ZnS crystals has emission peaks centered at blue region at 420 nm and 510 nm. For nano ZnS crystals the emission band was centered at 420 nm and 510 nm which arose from recombination of vacancies [5,22].

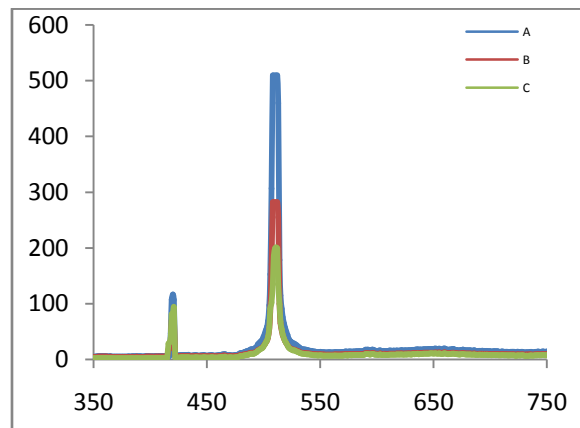


Fig. 3 Photoluminescence spectra of a-ZnS:Cu, b-ZnS nano, c-ZnS bulk at an excitation wavelength of 256 nm

After doping with Cu²⁺ ion, the luminescent centers were transferred to impurity ions. The transition metal ions have different d-d transitions, the emission peak of the Cu²⁺ doped sample was at about 510 nm. The PL intensity of Cu²⁺ doped ZnS sample is more as compared to pure ZnS. This could be explained by

impurity ions reducing electron-or hole-trapped surface levels on ZnS, leading to luminescence intensity increases [5,23-24].

IV CONCLUSIONS

The bulk, nano pure ZnS and Cu²⁺ doped ZnS nanoparticles were successfully synthesized by the chemical route technique, using SHMP as a capping agent. XRD pattern shows that the nanoparticles are in cubic zinc blend phase. Due to quantum confinement effect, band gap of the ZnS nanoparticles is increased in comparison to the bulk ZnS material. The PL spectrum showed that the ZnS nanoparticles has more intense peak as compared to the bulk ZnS and the intensity further increased after doping of Cu²⁺ ion. The PL spectra shows two peaks, first at 420nm and second at 510nm.

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